Supporting information for

A recipe for the synthesis of diorganotin(IV) phosphonates in colloidal regime by solution based approach

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Content

S1. **Materials and Methods**

Solvents were freshly distilled over magnesium cake (Methanol, ethanol). Glassware were dried in an oven at 110-120°C and further flame dried under vacuum prior to use. Triethylsilane, Phenyldimethylsilane, triethylphosphite, Allyl bromide and Karstedt's catalyst (Aldrich) were used as supplied. Literature methods were used to prepare diethyltinoxide and dimethyltinoxide.[1]

^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$ and $^{119}Sn\{^{1}H\}$ NMR spectra were recorded on a BRUKER DPX-300 spectrometer at 300, 75.48, 121.50, 119.92 MHz, respectively. ^{1}H and ^{13}C chemical shifts are quoted with respect to the residual protons of the solvents ($CDCl_3$) while ^{31}P and ^{119}Sn NMR data are given using 85% H_3PO_4 (aqueous) and tetramethyltin as the external standards, respectively. IR spectra were recorded on Nicolet protege 460 ESP spectrometer using KBr optics. Elemental analysis (C, H) was performed on a Perkin Elmer model 2400 CHN elemental analyzer. The electron spray mass (ESI-MS) spectra were recorded using a MICROMASS QUATTRO II triple quadruple mass spectrometer. The samples dissolved in chloroform/acetonitrile were introduced into the ESI source through a syringe pump at the rate of 5 $Lmin^{-1}$. The ESI capillary was set at 3.5 kV and the cone voltage was 40 V. Phase determination was done by using the powder XRD technique using CuKα radiation on a Bruker D8 advance machine. A scanning electron microscope (SEM) EVO-50 from Carl Zeiss AG, Germany was used to take images of the spin coated samples. Tapping mode atomic force microscopy (AFM) was carried out on a Bruker Dimension Icon AFM. The images were acquired in air by using a MPP-11100-10 probe (Bruker; tip radius and resonance frequency are 8 nm and 75 kHz respectively). HR-TEM Transmission electron microscopic (TEM) studies were carried out using a TECHNAI G2 (20S-TWIN) electron microscope. The solid state NMR spectra were recorded on a Bruker Avance II+ 600 NMR spectrometer operating at 600.11 MHz proton frequency (223.67 MHz for 119Sn),

using 4 mm solid state CP/MAS dual probehead. The samples were loaded in 4 mm zirconia rotors and spun at magic angle spinning (MAS) rates of 14 and 11 kHz to identify the isotropic chemical shift values. NMR spectra were measured with one-pulse sequence, 16K time domain data points, spectrum width of 2000 ppm, 6000 scans and a recycle delay of 5s. The spectra were referenced with respect to Me_4Sn as well as $SnCl_4$ as a secondary reference (isotropic chemical shift -145 ppm)

Synthetic methods

Synthesis of ligands, 1a and 2a

$Et_3Si(CH_2)_3P(O)(OH)_2$ (1a): Hydrosilylation reaction between diethylallylphosphonate, $C_3H_5P(O)(OEt)_2$ (5.28 g, 29.8 mmol) and triethylsilane (3.465 g, 29.8 mmol) in the presence of Karstedt's catalyst (10^{-6} Pt/mol of the silane)[2] (120 ºC, 48h) affords a clear liquid. The crude product was fractionally distilled and the fraction collected at 110-115 ºC/5torr was subjected to column chromatography on silica gel column using hexane-ethyl acetate (60:40) mixture to afford the isolation of the phosphonate diester, $Et_3Si(CH_2)_3P(O)(OEt)_2$ in analytically pure form. Subsequent hydrolysis of the phosphonate ester (4.0 g) was performed using 90mL of approximately 4N HCl solution under refluxed conditions for 24-30 h. The product was extracted in diethyl ether and dried over sodium sulphate. The removal of the solvent under vacuum affords a viscous liquid which was identified as **1a**.

$Et_3Si(CH_2)_3P(O)(OEt)_2$. Yield: 7.1 g, 82.0 %. ^{1}H NMR ($CDCl_3$): δ 4.04-3.98 (m, 4H, P-OCH_2-CH_3), 1.75-1.52 (br, 4H, P-CH_2CH_2), 1.25 (t, 6H, P-OCH$_2$CH_3), $^3J_{H\text{-}H}$ = 7.2 Hz), 0.85 (t, 9H, Si-CH$_2$CH_3, $^3J_{H\text{-}H}$ = 7.8 Hz), 0.55 (br, 2H, SiCH_2), 0.44 (q, 6H, SiCH_2CH$_3$, $^3J_{H\text{-}H}$ = 7.8 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 61.1 (d, P-O*C*H$_2$, $^2J_{P\text{-}O\text{-}C}$ = 6.1 Hz), 29.6 (d, P-*C*H$_2$, $^1J_{P\text{-}C}$ = 136.2 Hz), 17.1 (P-(CH$_2$)$_2$*C*H$_2$), 16.2 (P(OCH$_2$)*C*H$_3$), 13.0 (d, P(CH$_2$)*C*H$_2$, $^2J_{P\text{-}C}$ = 14.0 Hz), 7.2 (Si-*C*H$_3$), 3.0 (Si-*C*H$_2$). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 32.2. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ 6.1 (β-product, major), 8.0 (α-product, minor). ESI-MS (m/z): 295.1887 $[M+H]^+$, 317.1695

[M+Na]$^+$, 333.1447 [M+K]$^+$, 589.3758 [2M+H]$^+$, 611.3590 [2M+Na]$^+$, 627.3231 [2M+K]$^+$. IR (KBr, cm^{-1}): 2953, 2908 (ν_{C-H}), 1260 (ν_{Si-Me}), 1163, 1057 ($\nu_{P=O}$), 1028 (ν_{P-O-C}).

$Et_3Si(CH_2)_3P(O)(OH)_2$ (1a). Yield: 2.5 g, 78.0 %. ^{1}H NMR ($CDCl_3$): δ 8.76 (br, 2H, P(O)(O*H*)$_2$), 1.70-1.53 (br, 4H, PC*H*$_2$C*H*$_2$), 0.83 (t, 9H, Si-CH$_2$C*H*$_3$, $^3J_{H-H}$ = 7.8 Hz), 0.62-0.52 (br, 2H, Si-C*H*$_2$), 0.42 (q, 6H, Si-C*H*$_2$CH$_3$, $^3J_{H-H}$ = 7.8 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 29.9 (d, P-*C*H$_2$, $^1J_{P-C}$ = 133.9 Hz), 17.1 (P(CH$_2$)*C*H$_2$), 13.2 (P(CH$_2$)$_2$*C*H$_2$), 7.3 (Si(CH$_2$)*C*H$_3$}, 3.1 (Si-*C*H$_2$, $^1J_{Si-C}$ = 51 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 36.8. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ 6.4 (β-product, major), 8.5 (α-product, minor). ESI-MS (m/z): 237.109 [M-H]$^+$, 261.10 [M+Na]$^+$, 477.239 [2M+H]$^+$. IR (KBr, cm^{-1}): 2952, 2908, (ν_{C-H}), 1167, 1041 ($\nu_{P=O}$), 1237 (ν_{Si-Me}), 1008 (br) (ν_{P-O-H}).

$PhMe_2Si(CH_2)_3P(O)(OH)_2$ (2a). The synthesis of the phosphonate diester, $PhMe_2Si(CH_2)_3P(O)(OEt)_2$ was achieved by following a similar approach as described above using Pt-catalyzed hydrosilylation reaction between diethylallylphosphonate (5.28 g, 29.8 mmol) and phenyldimethylsilane (4.0 g, 29.8 mmol). The crude product was fractionally distilled at 110-125 ºC/ 5torr and further subjected to column chromatography on silica gel column using hexane-ethyl acetate (50:50) mixture. The phosphonate diester thus obtained (5.0 g, 15.9 mmol) was reacted with bromotrimethylsilane[3] (7.4 g, 47.9 mmol) in CH_2Cl_2 under ambient conditions and thereafter subjected to hydrolysis with de-ionized water. The organic layer was separated and dried over sodium sulphate. The solvent was removed under vacuum to afford **2a** as a white crystalline solid.

$PhMe_2Si(CH_2)_3P(O)(OEt)_2$. Yield: 6.9 g, 74.0 %. ^{1}H NMR ($CDCl_3$): δ 7.44 (m, 2H, Si-Ph), 7.28-7.26 (m, 3H, Si-Ph), 4.00-3.92 (m, 4H, P-OC*H*$_2$CH$_3$), 1.24 (t, 6H, P-OCH$_2$C*H*$_3$, $^3J_{H-H}$ = 7.2 Hz), 1.70-1.54 (br, 4H, P-C*H*$_2$C*H*$_2$), 0.81-0.75 (br, 2H, Si-C*H*$_2$), 0.20 (S, 6H, Si-C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 138.8 (C-1), 133.5 (C-2/C-6), 127.8 (C-3/C-5), 128.9 (C-4), 61.4 (d, P-O*C*H$_2$, $^2J_{P-C}$ = 6.3 Hz), 30.3 (d, P-*C*H$_2$, $^1J_{P-C}$ = 136.5 Hz), 17.5 {P-CH$_2$*C*H$_2$}, 17.3 (P-

$(CH_2)_2CH_2$), 16.5 (d, P-OCH_2CH_3, $^3J_{P-C}$ = 5.9 Hz), -2.75 (Si-CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 31.8. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ -3.5 (β-product, major), -1.4 (α-product, minor). ESI-MS (m/z): 313.1422 $[M-H]^+$, 337.1414 $[M+Na]^+$, 353.1145 $[M+K]^+$, 629.3098 $[2M+H]^+$, 651.2920 $[2M+Na]^+$. IR (KBr, cm^{-1}): 2960 (ν_{C-H}), 1256 (ν_{Si-Me}), 1163, 1055 ($\nu_{P=O}$), 1028 (ν_{P-O-C}).

$PhMe_2Si(CH_2)_3P(O)(OH)_2$ (2a). Yield: 4.1 g, 68.0 %. ^1H NMR ($CDCl_3$): δ 9.20 (br, 2H, P-O*H*), 7.48 (m, 2H, Si-Ph), 7.34 (m, 3H, Si-Ph), 1.77-1.66 (m, 4H, P-CH_2CH_2), 0.85 (m, 2H, Si-CH_2), 0.26 (s, 6H, Si-CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 138.8 (C-1), 133.5 (C-2/C-6), 128.9 (C-3/C-5), 127.8 (C-4), 29.0 (d, P-*C*H_2, $^1J_{P-C}$ = 141.8 Hz), 17.3 {P-CH_2CH_2}, 17.1 (P-$(CH_2)_2CH_2$), -3.1 (Si-*C*H_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 36.4. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ -3.4. ESI-MS (m/z): 281.0729 $[M+Na]^+$, 297.0478 $[M+K]^+$, 517.1760 $[2M+H]^+$, 539.1593 $[2M+Na]^+$. IR (KBr, cm^{-1}): 2952 (ν_{C-H}), 1255 (ν_{Si-Me}), 1210, 1166, 1142 ($\nu_{P=O}$), 1006 (ν_{P-O-H}).

Synthesis of diorganotin phosphonates 1-4.

In a typical procedure, the reaction of diethyltin oxide (0.34 g, 1.74 mmol) with phosphonic acid **1a** (0.41 g, 1.74 mmol) was performed under refluxing toluene for 12 h using a Dean and Stark apparatus. The solution was filtered to remove insoluble impurities. The solvent was removed from the filtrate under vacuum and methanol was added to precipitate a white solid which was filtered and dried under vacuum. The compound was identified as **1**. The compounds **2-4** were prepared by following a similar protocol using equimolar quantities of appropriate diorganotin oxide and the phosphonic acid.

$Et_2Sn\{O_3P(CH_2)_3SiEt_3\}$ (1). Yield: 0.45 g, 62.0 %. ^1H NMR ($CDCl_3$): δ 1.50-1.43 (br, 4H, PCH_2CH_2), 1.36-1.30 (m, 4H, Sn-CH_2), 1.20 (br, 6H, SnCH_3), 0.85 (t, 9H, Si-CH_2CH_3, $^3J_{H-H}$ = 7.8 Hz), 0.51 (br, 2H, Si-CH_2), 0.44 (q, 6H, Si-CH_2, $^3J_{H-H}$ = 7.8 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 34.0 (d, P-*C*H_2, $^1J_{P-C}$ = 140 Hz), 19.7 (Sn-*C*H_2), 18.9 ($P(CH_2)_2CH_2$, $^3J_{P-C}$ = 5.1 Hz), 13.8 (d, PCH_2CH_2, $^2J_{P-C}$ = 16.2 Hz), 9.5 ($SnCH_2CH_3$), 7.4 ($SiCH_2CH_3$), 3.3 (Si-*C*H_2).

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 13.7, 13.6 ($^{2}J_{Sn\text{-}O\text{-}P}$ = 145, 160 Hz). $^{119}Sn\{^{1}H\}$ NMR (CDCl3): δ -283 (q, $^{2}J_{Sn\text{-}O\text{-}P}$ = 160 Hz) ^{119}Sn MAS NMR: δ -283.4. IR (KBr, cm^{-1}): 1253 ($\nu_{Si\text{-}Me}$) 1102, 1045, 1012 (ν_{PO3}). Anal. Calcd for $C_{13}H_{31}O_3PSiSn$ (414.08): C, 37.79; H, 7.56; Found: C, 37.98; H, 7.65%.

***n*-Bu$_2$Sn{O$_3$P(CH$_2$)$_3$SiEt$_3$} (2)**. Yield: 0.54 g, 67.0 %. ^{1}H NMR ($CDCl_3$): δ 1.57-1.50 (br, 8H, PCH_2CH_2 + Sn-CH_2), 1.30-1.18 (br, 8H, Sn(CH_2)$_2$), 1.40-1.38 (br, 4H, Sn(CH$_2$)$_2$CH_2), 0.94 {(t, 9H, Si-CH$_2$CH_3 + 6H, Sn(CH$_2$)$_3$CH_3), 0.48 -0.40 (br, 8H, Si-CH_2 + Si-CH$_2$CH_3). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 33.7 (d, P-*C*H$_2$, $^{1}J_{P\text{-}C}$ = 140 Hz), 27.5 (Sn-*C*H$_2$), 27.2 (SnCH$_2$*C*H$_2$), 26.7 (Sn(CH$_2$)$_2$*C*H$_2$), 19.1 (P(CH$_2$)$_2$*C*H$_2$, $^{3}J_{P\text{-}C}$ = 4.5 Hz), 18.2 (d, PCH$_2$*C*H$_2$, $^{2}J_{P\text{-}C}$ = 15.8), 13.9 {Sn(CH$_2$)*C*H$_3$}, -2.9 (Si-*C*H$_3$). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 13.8, 13.7 ($^{2}J_{Sn\text{-}O\text{-}P}$ = 140 Hz). $^{119}Sn\{^{1}H\}$ NMR ($CDCl_3$): δ -281 (q, $^{2}J_{Sn\text{-}O\text{-}P}$ = 140 Hz). IR (KBr, cm^{-1}): 1102, 1041, 1017 (ν_{PO3}), 1259 ($\nu_{Si\text{-}Me}$). Anal. Calcd for $C_{17}H_{39}O_3PSiSn$ (470.14): C, 43.51; H, 8.38; Found C, 43.46; H, 8.42%.

Et$_2$Sn{O$_3$P(CH$_2$)$_3$SiMe$_2$Ph} (3). Yield: 0.51 g, 68.0 %. ^{1}H NMR ($CDCl_3$): δ 7.48 (m, 2H, Si-C$_6$H$_5$), 7.31 (m, 3H, Si-C$_6$H$_5$), 1.58-1.45 (br, 6H, PCH_2CH_2+Sn-CH_2), 1.34 (br, 6H, SnCH_3), 0.81 (m, 2H, Si-CH_2), 0.25 (S, 6H, Si-CH_3). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 139.4 (C-1), 133.5 (C-2/C-6), 128.9 (C-3/C-5), 127.8 (C-4), 33.6 (d, P-*C*H$_2$, $^{1}J_{P\text{-}C}$ = 141 Hz), 19.8 (Sn-*C*H$_2$), 19.1 (P(CH$_2$)$_2$*C*H$_2$, $^{3}J_{P\text{-}C}$ = 4.5 Hz), 18.2 (d, PCH$_2$*C*H$_2$, $^{2}J_{P\text{-}C}$ = 15.8), 9.5 (SnCH$_2$*C*H$_3$), -2.9 (Si-*C*H$_3$). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 13.9, 13.5 ($^{2}J_{Sn\text{-}O\text{-}P}$ = 145 and 160 Hz). $^{119}Sn\{^{1}H\}$ NMR ($CDCl_3$): δ -284 (q, $^{2}J_{Sn\text{-}O\text{-}P}$ = 160 Hz). IR (KBr, cm^{-1}): 1253 ($\nu_{Si\text{-}Me}$) 1094, 1045, 1004 (ν_{PO3}). Anal. Calcd for $C_{15}H_{27}O_3PSiSn$ (434.05): C, 41.59; H, 6.28; Found: C, 41.51; H, 6.35%.

Bu$_2$Sn{O$_3$P(CH$_2$)$_3$SiMe$_2$Ph} (4). Yield: 0.54 g, 63.0 %. ^{1}H NMR ($CDCl_3$): δ 7.43 (m, 2H, Si-C$_6$H$_5$), 7.26 (m, 3H, Si-C$_6$H$_5$), 1.55 (br, 8H, Sn-CH_2-CH_2), 1.32-1.18 (br, 8H, SnCH_2 + P-CH_2-CH_2), 0.92-0.76 (br, 8H, Si-CH_3 + P-CH$_2$), 0.25 (S, 6H, Si-CH_3). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 139.4 (C-1), 133.5 (C-2/C-6), 128.9 (C-3/C-5), 127.8 (C-4), 33.6 (d, P-*C*H$_2$, $^{1}J_{P\text{-}C}$

= 141 Hz), 19.8 (Sn-CH_2), 19.1 ($P(CH_2)_2CH_2$, $^3J_{P-C}$ = 4.5 Hz), 18.2 (d, PCH_2CH_2, $^2J_{P-C}$ = 15.8), 9.5 ($SnCH_2CH_3$), -2.9 (Si-CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 13.9, 13.5 ($^2J_{Sn-O-P}$ = 145 and 160 Hz). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$): δ -284 (q, $^2J_{Sn-O-P}$ = 160 Hz). ^{119}Sn MAS NMR: δ -283. IR (KBr, cm^{-1}): 1253 (ν_{Si-Me}) 1095, 1042, 1020 (ν_{PO3}). Anal. Calcd for $C_{19}H_{35}O_3PSiSn$ (490.12): C, 46.64; H, 7.21; Found: C, 46.48; H, 7.34%.

Synthesis of $Sn\{O_3P(CH_2)_3SiR^1R^2_2\}_2$ [$R^1 = R^2$ = Et (5); R^1 = Ph, R^2 = Me (6)]

The reaction between dimethyltin oxide (0.28 g, 1.74 mmol) and silaalkylphosphonic acid, **1a** (0.82 g, 3.48 mmol) or **2a** (0.89 g, 3.48 mmol) was performed under similar conditions as described above for **1**. The solid thus obtained was analyzed as **5** and **6**.

$Sn\{O_3P(CH_2)_3SiEt_3\}_2$ (5). Yield: 0.60 g, 59.0 %. ^1H NMR ($CDCl_3$): δ 1.25 (br, 4H, PCH_2CH_2), 0.85 (br, 9H, $SiCH_3$), 0.45 (br, 8H, Si-CH_2 + Si-CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 30.5 (d, P-CH_2, $^1J_{P-C}$ = 143 Hz), 17.6 ($P(CH_2)_2CH_2$), 13.2 (PCH_2CH_2), 7.4 ($SiCH_3$), 3.2 (Si-CH_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 25.4, 18.2. $^{119}Sn\{^1H\}$ NMR ($CDCl_3$): δ -601. ^{119}Sn MAS NMR: δ -680. IR (KBr, cm^{-1}): 1254 (ν_{Si-Me}) 1095, 1062, 1014 (ν_{PO3}). Anal. Calcd for $C_{18}H_{42}O_6P_2Si_2Sn$ (592.10): C, 36.56; H, 7.16; Found: C, 36.59; H, 7.35%.

$Sn\{O_3P(CH_2)_3SiMe_2Ph\}_2$ (6). Yield: 0.62 g, 56.0 %. ^1H NMR ($CDCl_3$): δ 7.48 (m, 2H, Si-C_6H_5), 7.32 (m, 3H, Si-C_6H_5), 1.62 (br, 4H, P-CH_2-CH_2), 0.82 (br, 2H, Si-CH_2), 0.26 (S, 6H, Si-CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 30.5 (d, P-CH_2, $^1J_{P-C}$ = 143 Hz), 17.4 ($P(CH_2)_2CH_2$), 17.1 (PCH_2CH_2), -3.1 (Si-CH_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 25.9, 18.4. $^{119}Sn\{^1H\}$ NMR ($CDCl_3$): δ -604. IR (KBr, cm^{-1}): 1250 (ν_{Si-Me}) 1094, 1064, 1014 (ν_{PO3}). Anal. Calcd for $C_{22}H_{34}O_6P_2Si_2Sn$ (632.04): C, 41.85; H, 5.43; Found: C, 41.72; H, 5.49%.

Synthesis of colloidal particles derived from 1, 2 and 5

To transform the bulk samples into colloidal domain, as synthesized polymers (5.0 mg) were dispersed separately in ethanol-chloroform (5:1) mixture (5.0 mL) and the resulting solution in each case was ultrasonicated. The insoluble solid was allowed to settle down for a few

hours and the transparent supernatant was separated. The resulting solution exhibits Tyndall effect suggesting the formation of colloidal particles.

S2. NMR Data

Fig. 1 ^{31}P NMR spectrum of $Et_2Sn\{O_3P(CH_2)_3SiEt_3\}$ **1**.

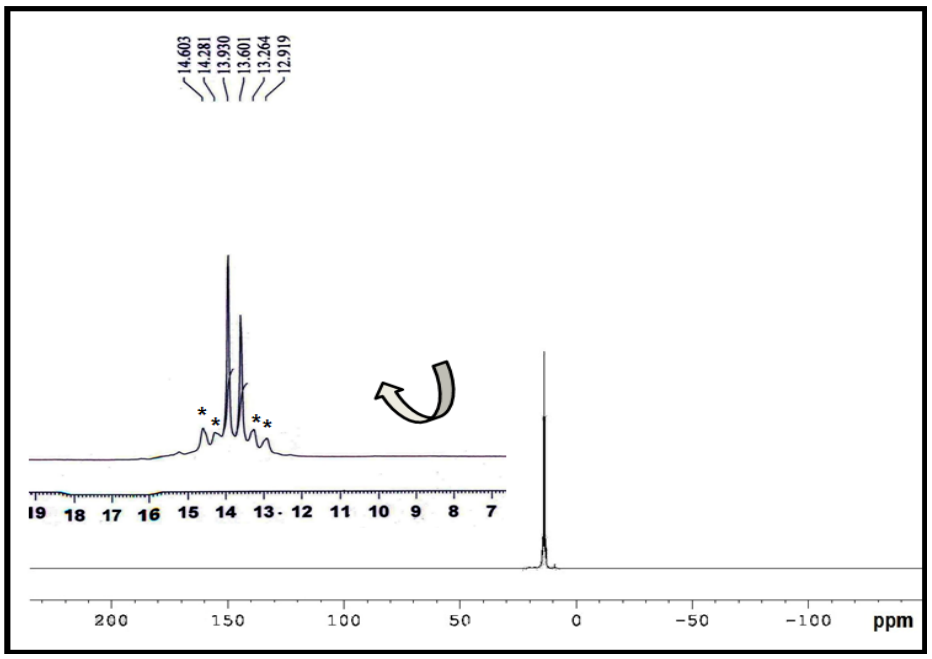


Fig. 2 ^{119}Sn NMR spectrum of $Et_2Sn\{O_3P(CH_2)_3SiEt_3\}$ **1**.

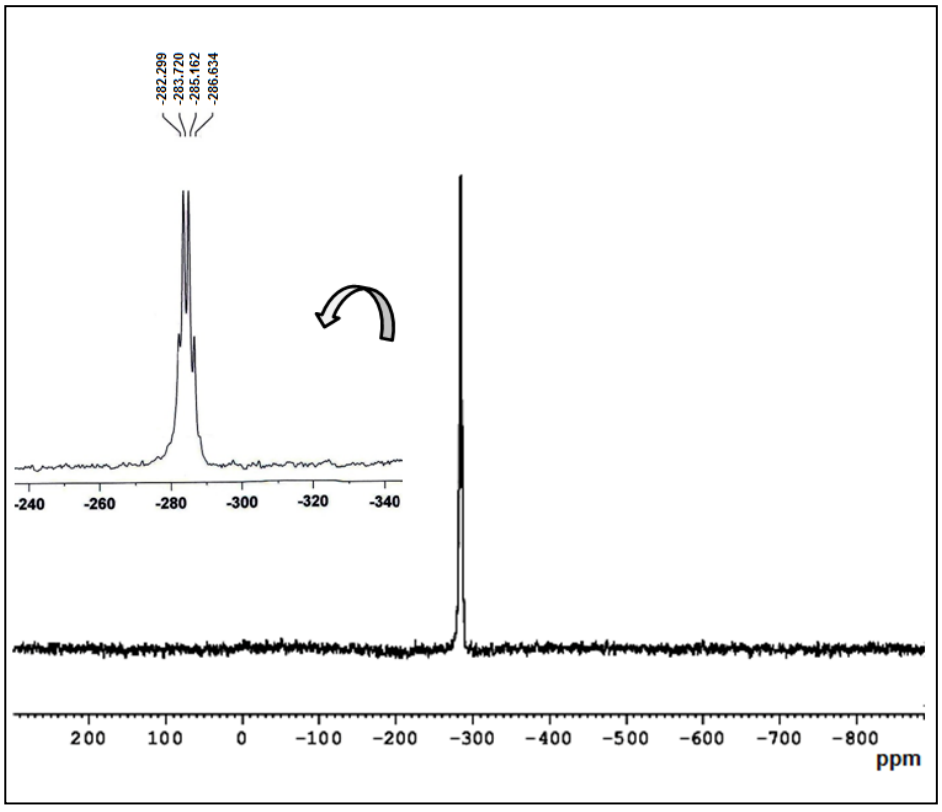


Fig. 3 ^{119}Sn

solid state NMR spectra of $Et_2Sn\{O_3P(CH_2)_3SiEt_3\}$**1** measured at 14 kHz and 11 kHz. The isotropic chemical shift at -283.4 ppm is indicated with an arrow.

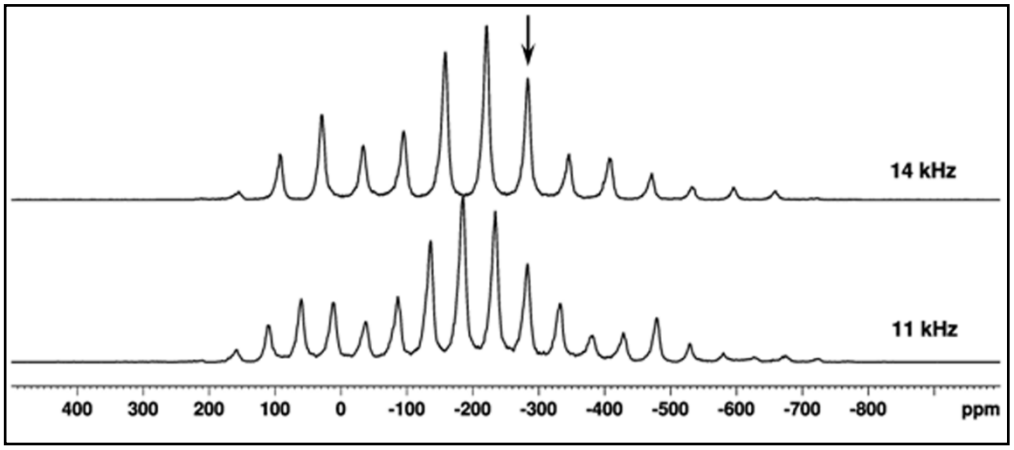


Fig. 4 ^{119}Sn solid state NMR spectra of *n*-$Bu_2Sn\{O_3P(CH_2)_3SiPhMe_2\}$**4** at 14 kHz and 11 kHz. The isotropic chemical shift at around -283 ppm is indicated with an arrow.

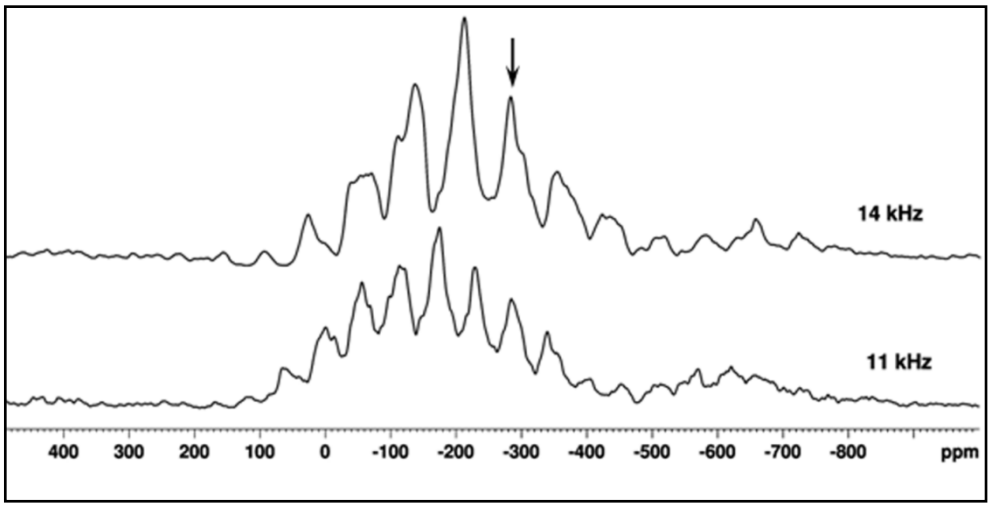


Fig. 5 ^{1}H NMR spectrum of $Sn\{O_3P(CH_2)_3SiEt_3\}_2$ **5**.

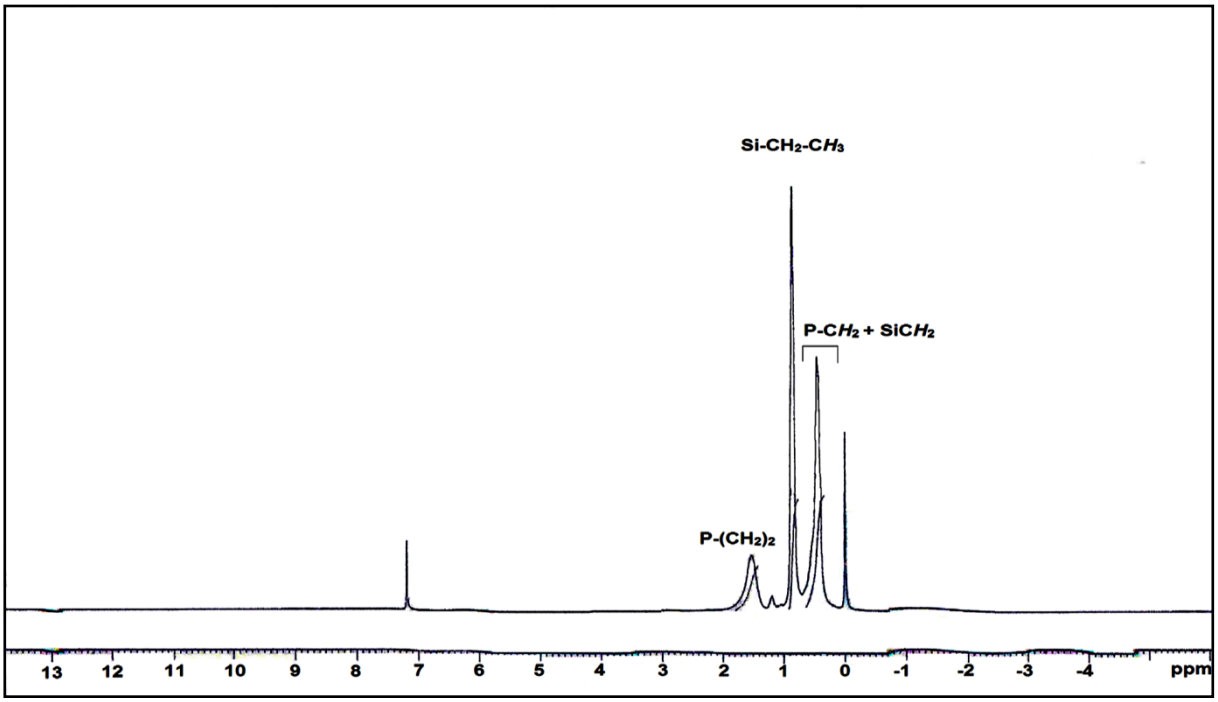


Fig. 6 DEPT-135 NMR spectrum of $Sn\{O_3P(CH_2)_3SiEt_3\}_2$ **5**.

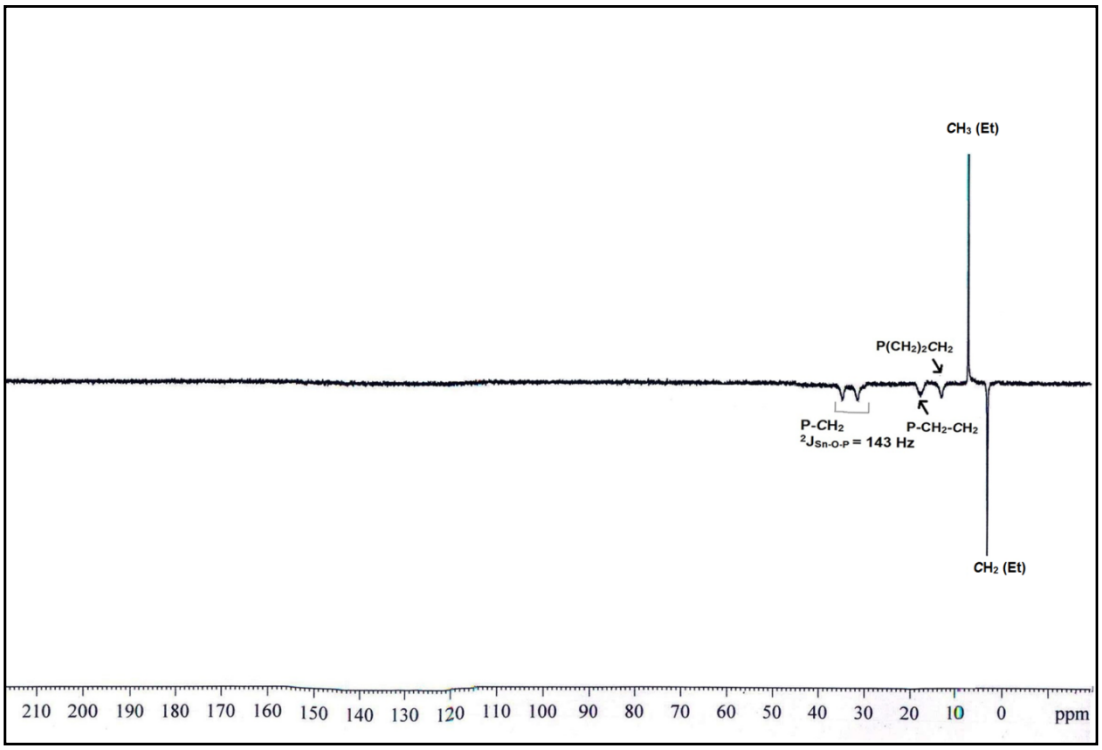


Fig. 7 ^{119}Sn solid state NMR spectra of $Sn\{O_3P(CH_2)_3SiEt_3\}_2$ **5** at 14 kHz and 11 kHz. The isotropic chemical shift at around -680 ppm is indicated with an arrow.

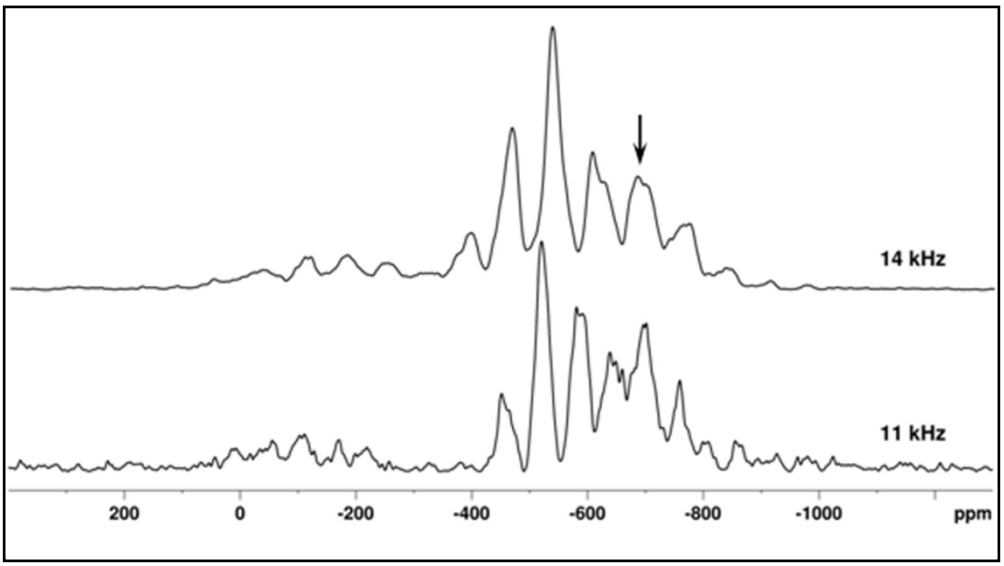


Fig. 8 ^{119}Sn NMR spectrum of $Sn\{O_3P(CH_2)_3SiEt_3\}_2$ **5**.

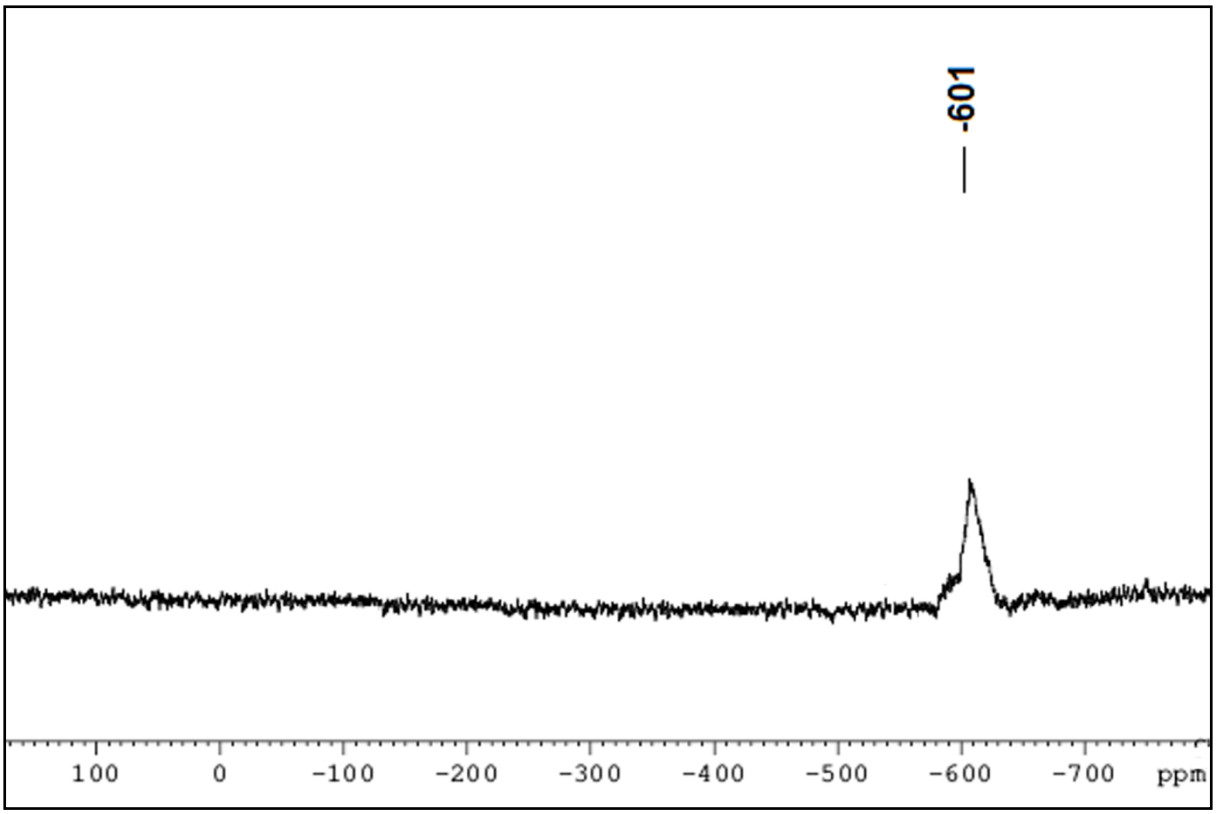
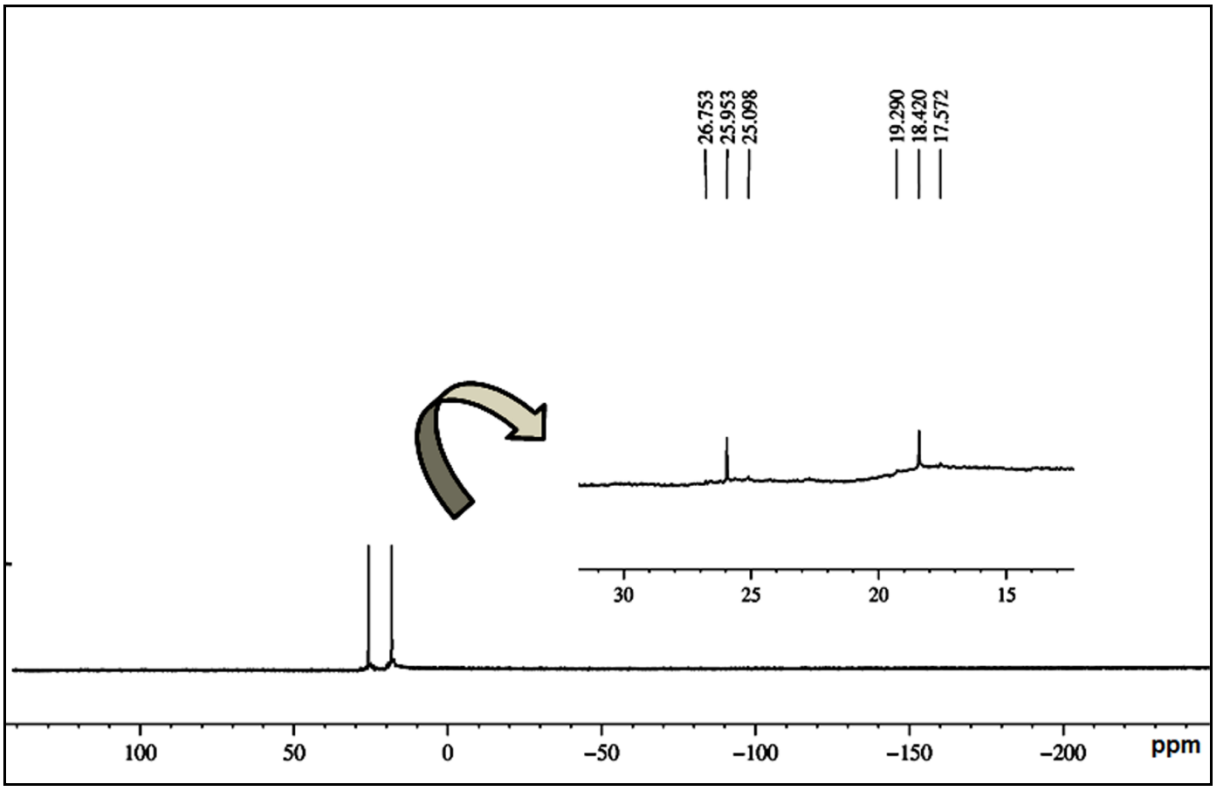


Fig. 9 ^{31}P NMR spectrum of $Sn\{O_3P(CH_2)_3SiPhMe_2\}_2$ **6**.



S3. Powder X-ray diffraction pattern

Fig. 1 Powder X-ray diffraction pattern of $Et_2Sn\{O_3P(CH_2)_3SiEt_3\}$ **1**. The Crystallographic information file (CIF) of *n*-$Bu_2Sn(O_3PPh)$ (CCDC No. 737802) was used for indexing.

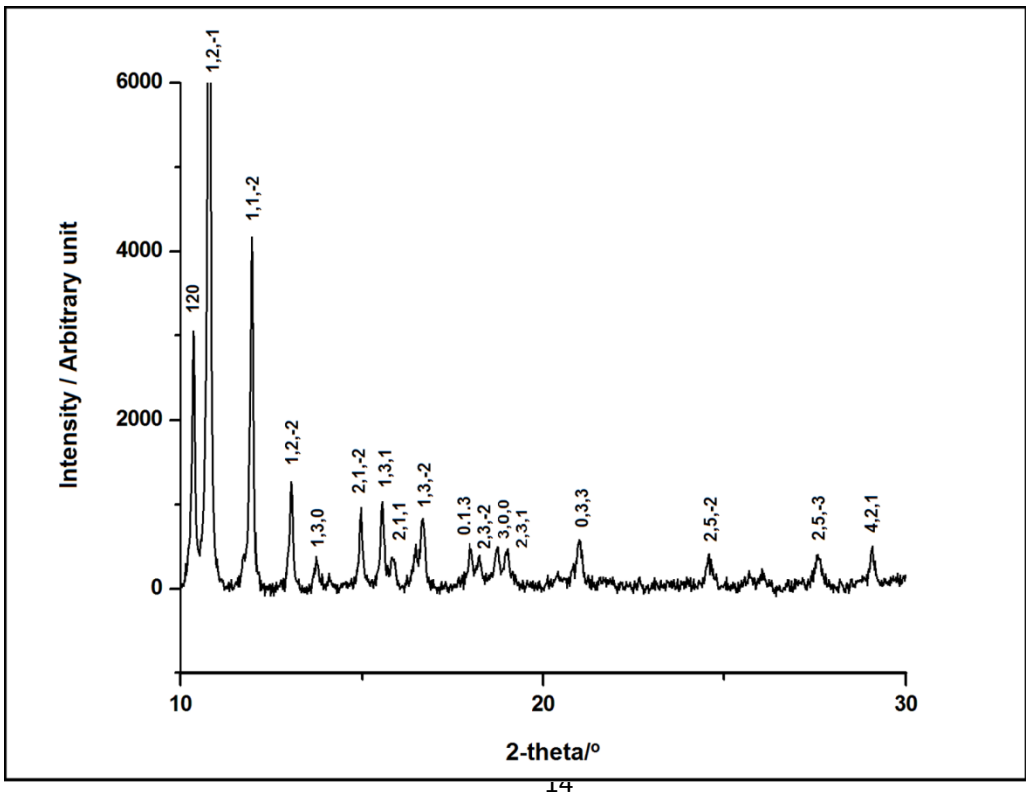
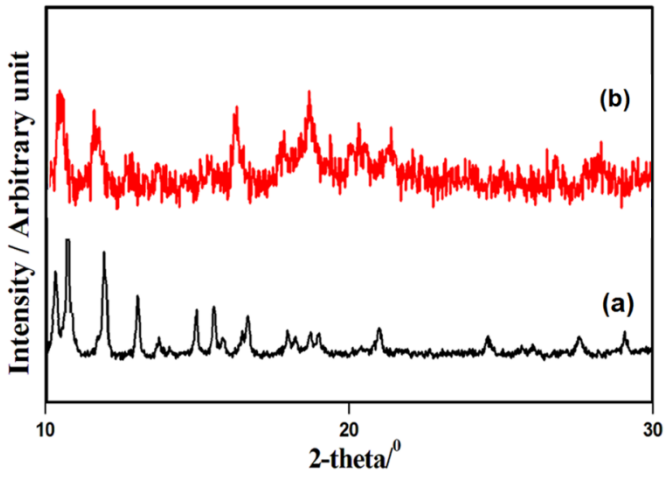
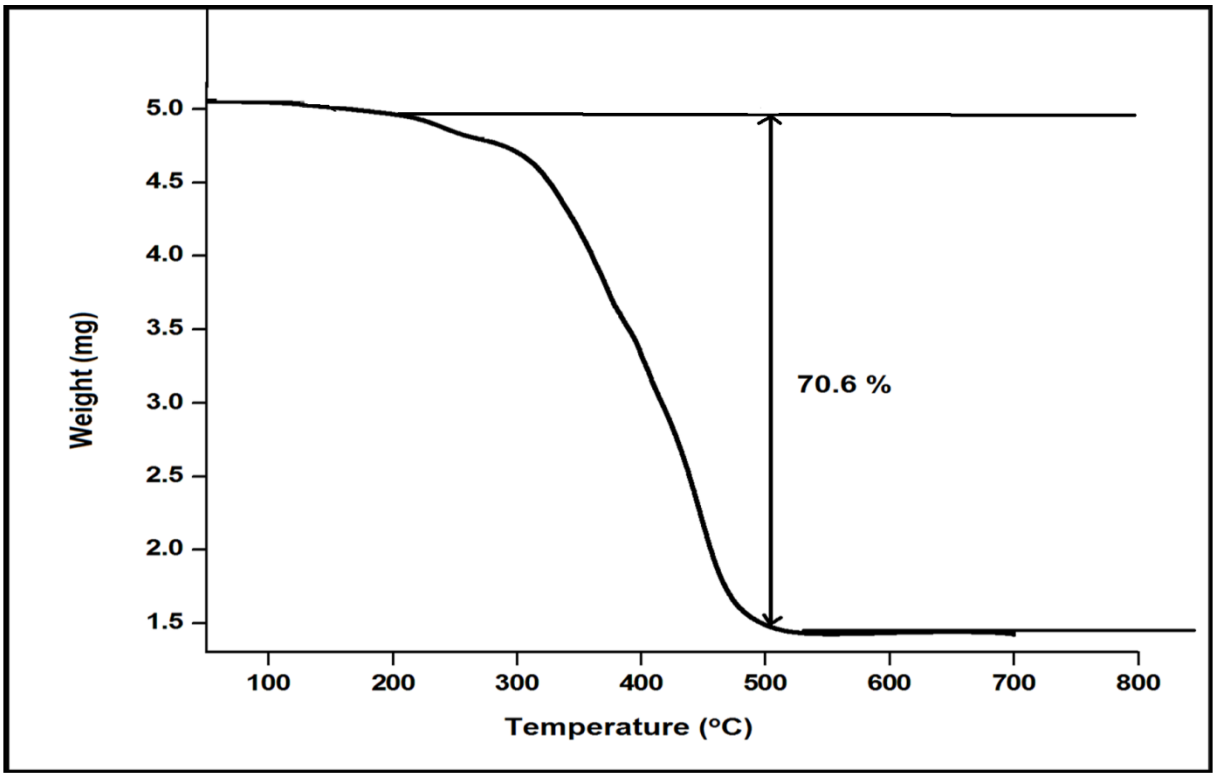


Fig. 2 Powder X-ray diffraction pattern of $Et_2Sn\{O_3P(CH_2)_3SiEt_3\}$ **1**. (a) as synthesized sample (b) after immersing in water for 24h.

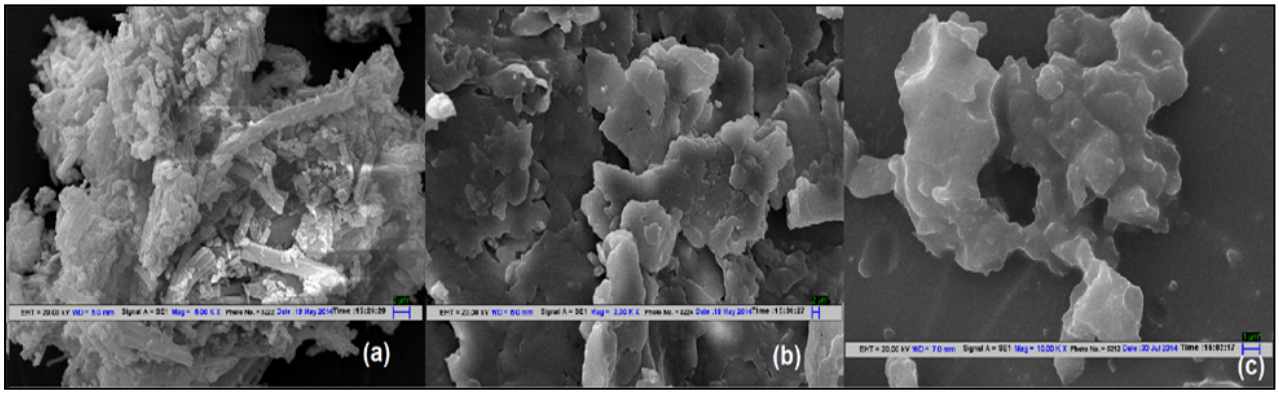


S4. TGA curve of $Bu_2Sn\{O_3P(CH_2)_3SiEt_3\}$ **2**.



S5. Tyndall effect of colloidal particles of *n*-$Bu_2Sn\{O_3P(CH_2)_3SiEt_3\}$ **2**.

S6. SEM micrographs of as synthesized (a) **3**, (b) **4** and (c) **6** respectively



S7. Antibacterial Studies

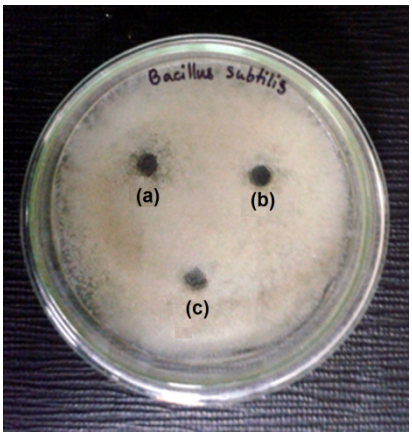
The media components used for culturing were procured from Hi Media Laboratory, Mumbai, India. Nutrient broth was used for culturing the bacterial strains. The bacterial cultures used for antibacterial activity experiment were those of wild type gram positive strain of *Bacillus subtilis*. For preliminary screening of the antimicrobial activity of the compounds agar well diffusion method was followed. Petri plates containing 25.0 mL of Nutrient agar were seeded with 24 h culture of bacterial strains of *B. subtilis* and *pseudomonas aeruginosa*. Wells were cut and 100 µL of the colloidal solution of ligands **1a** and **2a** as well as organotin phosphonates **1-6** (concentration 1.0 mg/mL) were added. The

plates were then incubated at 30°C for overnight. The antibacterial activity was assayed by measuring the radius of the inhibition zone formed around the well.

1. Table of Antibacterial Data

Compound/Solvent	***Results of growth inhibition***	
	Bacillus subtilis	***Pseudomonas aeruginosa***
1 (Bulk)	No inhibition. Matted growth of bacterial culture obtained.	No inhibition.
1 (Nano)	Yes, a small zone of inhibition was obtained. Radius 1mm.	No inhibition.
2 (Bulk)	No inhibition. Matted growth of bacterial culture obtained.	No inhibition.
2 (Nano)	Yes, a small zone of inhibition was obtained. Radius 4mm	No inhibition.
3 (Bulk)	No inhibition. Matted growth of bacterial culture obtained.	No inhibition.
4 (Bulk)	No inhibition. Matted growth of bacterial culture obtained.	No inhibition.
5 (Bulk and Nano)	No inhibition. Matted growth of bacterial culture obtained.	No inhibition.
6 (Bulk)	No inhibition. Matted growth of bacterial culture obtained.	No inhibition.
Ligand **1a**	No inhibition. Matted growth of bacterial culture obtained.	No inhibition.
Ligand **2a**	No inhibition. Matted growth of bacterial culture obtained.	No inhibition.
S_1(Chloroform)	No inhibition. Matted growth of bacterial culture obtained.	No inhibition.
S_2(Ethanol + Chloroform)	No inhibition. Matted growth of bacterial culture obtained.	No inhibition.

2. Inhibition Zone for phosphonic acids (a) **1a** and (b) **2a** (c) Chloroform



S8. References

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2. R. Shankar, V. Shahi and U. Sahoo, *Chem. Mater.* 2010, **22**, 1367.
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